# AN EXPERIMENTAL INVESTIGATION INTO THE USE OF MOLTEN CARBONATE FUEL CELLS TO CAPTURE $CO_2$ FROM GAS TURBINE EXHAUST GASES

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## ABSTRACT

As part of its climate change mitigation initiative, BP is evaluating technologies for the separation and capture of $CO_2$ from combustion sources, for subsequent geologic storage. Ansaldo Fuel Cells S.pA. is developing Molten Carbonate Fuel Cell (MCFC) technology targeted at industrial applications from 50 kW to 10MW. This paper describes the conceptual design of a hybrid MCFC system to generate power and simultaneously capture $CO_2$ from small (<10MW) gas turbine exhaust streams. Modeling studies have shown that a 1.6MW MCFC could reduce the $CO_2$ emissions from a 4.6MW gas turbine by 50% on a per kWh basis, assuming suitable sequestration of the concentrated $CO_2$ from the fuel cell. Subsequent experimental studies have confirmed that the fuel cell can operate at below-design $CO_2$ levels of 3-4% typical of exhaust gas streams, with limited loss in power and efficiency. We also determined that the presence of NOx has only a minor suppressing effect on performance. This technology could offer a unique solution to capturing significant amounts of $CO_2$ from small, distributed power generation facilities.

## INTRODUCTION

BP is seeking solutions to the climate change challenge. This includes controlling emissions, conserving energy and introducing new energy-efficient technologies. One such technology, hydrogen fuel cells, offers the potential for highly efficient power generation at a scale (<10MW) widely employed in the oil and gas industries. This could replace today's technology including small gas turbines and large diesel or gas fired reciprocating engines, often operating at part load efficiencies below 30%.

In addition, as part of our $CO_2$ mitigation initiative, BP is evaluating technologies for the separation and capture of $CO_2$ from combustion sources for subsequent storage. At present, commercially viable technologies are not available at scale. A portfolio of innovative options is needed, which include technologies that allow us to take constructive action in the medium term (next 5-10 years).

One such innovative idea is to exploit the ability of molten carbonate fuel cells to transport $CO_2$ across the electrolyte. In the medium term, we can envisage that many facilities will still possess a considerable number of conventional power generating technologies operating in parallel with fuel cells.

Ansaldo Fuel Cell S.p.A. is considering the possibility of hybridizing their molten carbonate fuel cell technology with gas turbines to capture $CO_2$ from the exhaust streams of such conventional technologies by feeding the $CO_2$ to the cathode, while still generating power at high efficiency [1]. Although this innovative concept is feasible in principle and confirmed by system modeling, BP and Ansaldo embarked on an extensive experimental study to determine the system behaviour, operating envelope and the impact of contaminants.

This paper presents the final results and conclusions from this successful collaborative project.

## DISCUSSION OF THE TECHNOLOGY

### *Ansaldo's Molten Carbonate Fuel Cell Technology*

Ansaldo Fuel Cell S.p.A. (formerly part of Ansaldo Ricerche) has been developing Molten Carbonate Fuel Cell (MCFC) technology since the early 1980's. The next generation, "Series 500" power plant represents the latest step in the development of this MCFC technology. The plant will generate power at high efficiency, with low environmental impact and rapid response to load changes. The target market is on-site dispersed energy production for small to medium scale, commercial & industrial customers (circa 50KW to several MW).

The Series 500 fuel cell development is based on the achievements of the previous phase of the development programme, in particular:-

- Operation of a 100KW "proof of concept" power plant performed at an ENEL site near Milan (Italy) during 1998-99

- Operation of a full area rectangular stack (an improvement over the square stack used in 100KW plant) under different operating conditions performed in the stack test and conditioning facility in the IBERDROLA site of S.A. de Guadalix, near Madrid (Spain)

The heart of the Series 500 is based on two electrochemical modules, each formed by two stacks integrated with their relevant auxiliary systems and coupled according to the original TWINSTACK® configuration. Currently, the first-of-a-kind unit is under development and other contracts have been received or are being negotiated for the demonstration of a stack module fed by a biomass gasifier, a diesel fed Series 500 unit, and a landfill-gas fed Series 500.

When compared with traditional power plant solutions of equivalent size, the main issues relating to TWINSTACK® competitiveness in terms of performance are:

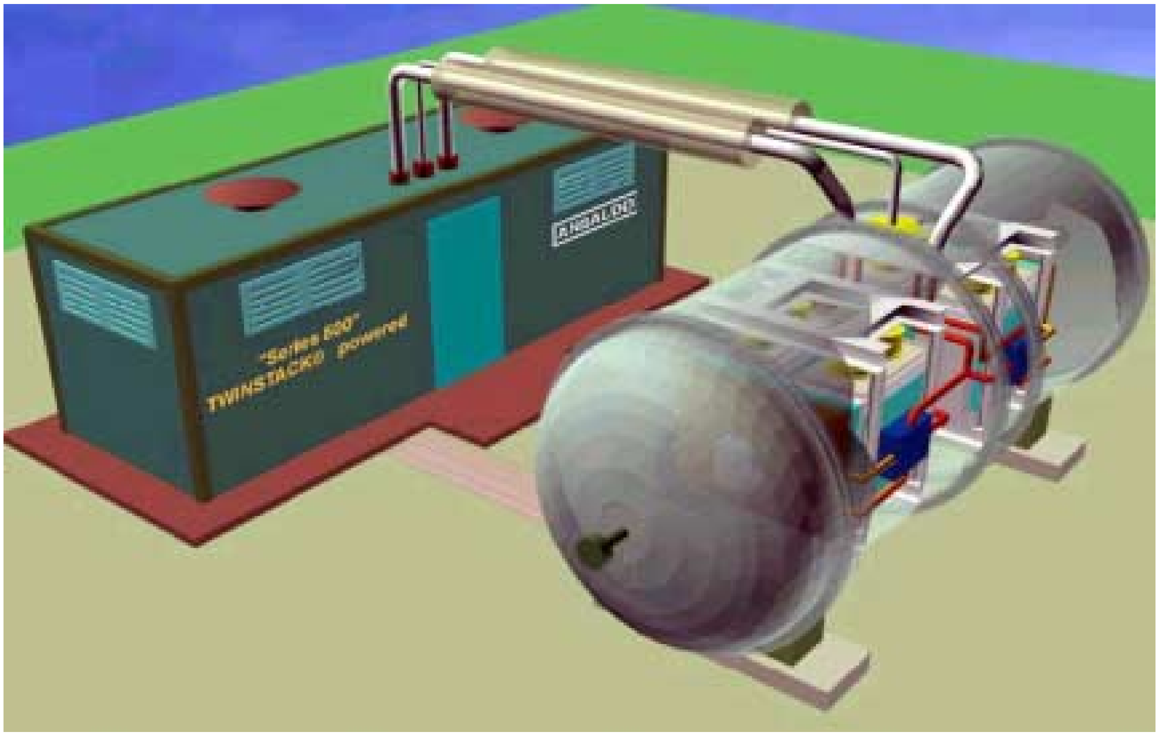
- Overall size reduction, by locating key components inside a suitable vessel

- Reduction of the number of components

- Simplification of the maintenance procedures and reduction of the service time

- Optimization of the layout in a skid-mounted solution, for ease of installation.

The Series 500 unit will also be used as the "building-block" for larger scale, multi MW power plants. In these designs, the system will be optimized, by suitable integration of some balance of plant (BoP) components, in order to reduce footprint and costs. The plant adopts a skid-mounted compact design, where the stacks, integrated reformers and catalytic burners are located inside a single pressurized vessel. All other auxiliary systems (including power conditioning and control systems) are installed on a separate skid.




Schematic: Ansaldo Series 500 MCFC

Fuel Cells are devices that directly convert the chemical energy of a fuel, typically hydrogen, into electrical energy, by electrochemical reactions. Molten Carbonate Fuel Cells (MCFC) are high temperature systems (Tm≅ 650 °C) suitable for power generation at commercial/industrial scale (>50 kW). Figure 1 is a simple schematic of the technology.

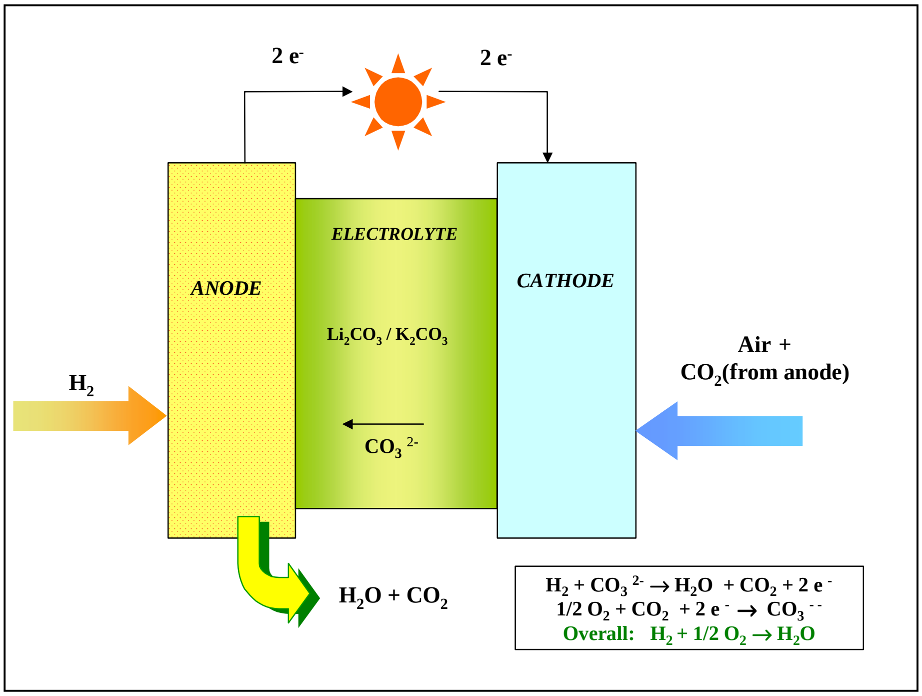


Figure 1: Molten Carbonate Fuel Cell Scheme

When $H_2$ is fed to the anode side, it combines with the carbonate ions of the electrolyte to form steam and carbon dioxide and provides electrons as DC current. This DC current is normally inverted, using solid-state electronics, to produce AC for an external load. Simultaneously, the oxygen from the air and carbon dioxide (a slipstream from the anode reactions) are fed to the cathode, and react to replenish the carbonate ions consumed at the anode.

The $H_2$ is produced by the steam reforming of methane (natural gas). This reaction together with the shift reaction ultimately generates $CO_2$ via CO. To ensure optimization of system efficiency, Ansaldo has heat integrated this process with the fuel cell reactions. Consequently, the fuel cell can generate electricity at high overall efficiencies, well above 40% for the complete system, methane to electricity.

Another environmentally beneficial characteristic of the MCFC technology is its ability to transport carbon dioxide across the electrolyte, from the cathode side to the anode side of the fuel cell. Present on the anode side are typically $H_2$, CO, $CO_2$ and $H_2O$. At the anode exit the gas composition includes un-reacted $H_2$, steam and concentrated $CO_2$ (from the cathode transfer and the reformate). The steam can be readily condensed, $H_2$ can be separated and the residual $CO_2$ is therefore available as a relatively pure stream for sequestration. It is this characteristic that we wish to exploit.

***The Hybrid Fuel Cell Scheme for $CO_2$ Capture***

The innovative scheme being proposed is a fuel cell hybrid based around Ansaldo's molten carbonate technology and a typical gas turbine. The aim of this integration is to maintain power generation on an existing gas turbine but ultimately with much reduced $CO_2$ emission to the atmosphere. The use of MCFC will provide not only additional power generation capability at an increased level of efficiency, but also the means for concentrating and separating the $CO_2$ from the conventional gas turbine. The exhaust from such a turbine would typically contain between 3 and 4%vol $CO_2$. Overall, we believe that circa 50-60% of the $CO_2$ emissions of conventional power plants could be separated with this scheme.

In this study we have chosen to focus on a typical natural gas fired, small industrial gas turbine of nominal power output of 4.6 MW at standard operating conditions (15 degC, normal pressure at sea level). At this scale a single turbine would be generating over 3 tonnes per hour of $CO_2$ (i.e. over 25000 tonnes per annum).

We have also considered both an atmospheric and pressurized fuel cell system. A pressurized system can offer performance benefits in the fuel cell, notably increased power output that may generate additional value for the overall scheme. However, for the purposes of describing the concept, it suffices to focus on the atmospheric scheme (Figure 2).

This hybrid concept has been modeled using Ansaldo's in-house expertise, based on several years of MCFC technology development and optimization. This includes not only the electrochemical processes of the cell, but also the engineering parameters such as pressure drop and heat integration.

In our hybrid scheme, we have determined that the exhaust from a conventional 4.6 MW gas turbine can be fed to the cathode of a 1.6 MW atmospheric MCFC system. We believe that this ratio of between 2:1 and 3:1 in the relative power outputs of the two technologies in the hybrid scheme is scaleable e.g. a 10 MW gas turbine could be coupled with a fuel cell system in the 3 to 5 MW range.

At the cathode, as a result of the electrochemical reaction with exhaust oxygen, the $CO_2$ reacts to form carbonate ions and the resulting content of $CO_2$ in the turbine exhaust stream is reduced from 4.7%wt (~3%vol) down to 2.3 wt% (~1.5%vol) i.e. a reduction of 50% across the fuel cell.

Following transport of the carbonate ions across the electrolyte to the anode, the $CO_2$ is released and mixed with the components from the reforming process ($H_2$, CO and a small quantity of unconverted $CH_4$). At the anode, the $CO_2$ content of the reformate is increased from ~25%wt at the inlet to ~55%wt at the outlet. On a dry basis, this corresponds to a concentration of $CO_2$ of about 85%wt. This anode exhaust, composed mainly of $H_2O$ and $CO_2$, with some $CH_4$, $H_2$ and CO, is directed to a $CO_2$ separation unit; the steam is condensed and the $CO_2$ is separated for subsequent storage.

The residual gas (CO, $H_2$, and $CH_4$) from this $CO_2$ separation process is then recombined with the cathode off-gas in the catalytic burner, before release to the atmosphere. The combustion of CO in the catalytic burner generates additional $CO_2$ in this exhaust stream, which obviously diminishes the overall reduction of the emissions. Nevertheless, in this un-optimized scheme, the $CO_2$ released to the atmosphere can be reduced by circa 40% (i.e. from 3.2 tonnes per hour to 2.0 tonnes per hour, equivalent to a reduction of circa 10500 tonnes per annum). If we then consider that the MCFC is also generating 1.6MW of power in addition to the gas turbine's 4.6 MW, then the $CO_2$ emission per kWh produced is reduced by over 50%.

These initial results gave us confidence that the MCFC hybrid system can act as a carbon dioxide concentrator [2].

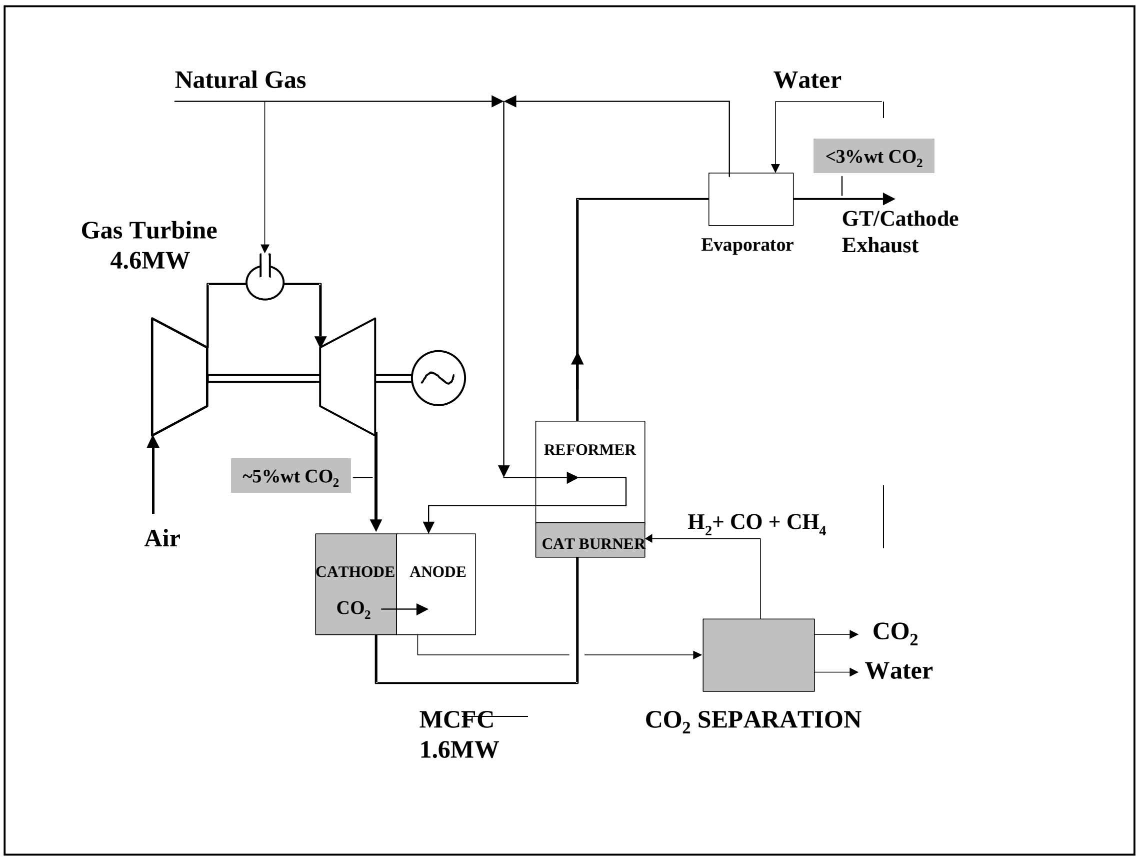



Figure 2. Hybrid Atmospheric Pressure MCFC Scheme for $CO_2$ Capture

## EXPERIMENTAL STUDIES

***Work Programme Objectives***
The experimental investigation was carried out at Ansaldo Fuel Cell S.p.A.'s test facilities in Genova, Italy. The work programme has quantified:

- The effect on the baseline fuel cell performance of varying $CO_2$ concentrations at the cathode
- Impact of operating pressure on the system
- The effect of contaminants on performance and lifetime

The experiments were performed on single cells. The results can then be readily and reliably extrapolated to a large-scale fuel cell system.

***Experimental Results***
Any exhaust from a conventional combustion process can be considered as a source of $CO_2$ for this fuel cell hybrid. However, the concentration of $CO_2$ at the cathode is critical to the performance of the fuel cell, particularly if levels fall too low. Consequently, we have been quantifying the effect of varying $CO_2$ levels on the fuel cell power output and $CO_2$ transport across the electrolyte.

In the above scheme, such gas turbines are fuelled either by natural gas (methane) or by No.2 fuel oil (diesel), and often employ dry low NOx burners to reduce emissions. The major constituents of the exhaust from such a turbine are Nitrogen ($N_2$) 75%, Oxygen ($O_2$) 14%, Water ($H_2O$) 4 to 7% and Carbon Dioxide ($CO_2$) 3 to 4% by volume.

The results from these single atmospheric cell studies are illustrated in Figure 3 and were reported previously [3]. For a stand-alone molten carbonate fuel cell, $CO_2$ levels at the cathode are typically maintained at circa 7-8%vol. At this concentration, the power density for a single cell was measured at circa 740 $W/m^2$ and the voltage at around 800 mV. This would correspond to an overall power output of 1.6MW for the MCFC unit alone (i.e. excluding the gas turbine power generation).

Concentrations of $CO_2$ above 7%vol were found to deliver only limited improvements in power density.

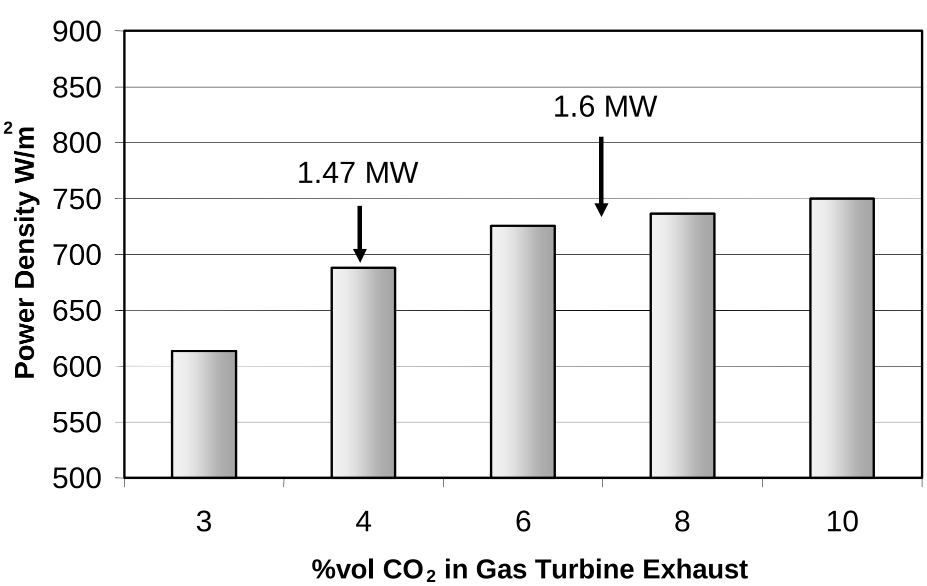



Figure 3. Single Cell Experimental Results

At the lower, sub-optimal concentrations (<7%vol $CO_2$) typical of gas turbine exhaust streams, the power density of the cell was found to decline. At 4%vol $CO_2$, the power density was approximately 690W/m2, which can be extrapolated to circa 1.47 MW for the MCFC system. At 3%vol $CO_2$, the power density declined towards 610 W/m2, equivalent to around 1.3MW. These experimental results confirm the concept's feasibility and that, under these conditions, it would be possible to reduce the $CO_2$ emission per kWh produced by circa 45% at the 4%vol $CO_2$ and by circa 50% at the 3%vol $CO_2$.

Only at $CO_2$ levels of 2%vol did the power density fall away dramatically and therefore have a significant and deleterious effect on overall performance.

Relative to that measured under atmospheric conditions, operation of the cell at pressure (3.5 bara) demonstrated that a 15% increase in power output is achievable, even at the sub-optimal $CO_2$ level of 3%mol. Under these conditions $CO_2$ reduction was determined at 55%. Increasing the current density (at the expense of some power output) helped to increase the $CO_2$ transfer rate and therefore removal from the gas turbine exhaust stream. In this test a figure of 59% reduction was achieved.

***Comparison with Modeling Results***

The performance data predicted by the modeling work were shown to be close to those actually observed in the experiments. This gives us confidence in our design parameters and our ability to model innovative system designs. The following table compares some of the predicted and actual data:-

| | Model Prediction | Experimental Results |
|---|---|---|
| MCFC Power | 1.6 MW | 1.3 – 1.5 MW |
| $CO_2$ transferred to anode | 55% | 48% |
| $CO_2$ at the anode exit | 53%mol (dry) | 51%mol (dry) |
| Current Density | 1000 A/m2 | 909 A/m2 |

***Impact of Contaminants***

The presence in the exhaust gas streams of any contaminants for the fuel cells is a cause for concern as they have the potential to degrade both performance and lifetime. In this study, we focused on the effect that the presence of both SOx and NOx will have on the operation of the MCFC.

The harmful effects of nitrogen oxides has been identified in the past but not quantified. Our experiments determined the impact of 25 ppm of NO in the cathode gas on the performance of the MCFC, over an extensive period of circa 500 hours. We also investigated the ability of the fuel cell to recover from exposure to such a contaminant.

These results indicate that the effect, although detrimental, is not significant – a 2.5% reduction in performance. The experiment also indicated that the effect is reversible – that after removal of NOx from the gas stream, the fuel cell performance returned to normal with no onbvious detrimental impact.

In contrast as the MCFC can act as a sulphur scrubber, $SO_2$ is known to accumulate in the electrolyte as sulphate, and readily transferred to the anode where it can react with the hydrogen to form $H_2S$. This in turn has a strong poisoning effect on the nickel based anodes. However, we believe this issue can be managed with suitable pretreatment if needed.

## CONCLUSION

Our study has concluded that MCFC technology has the potential to be integrated in a combined power generation and $CO_2$ concentrator hybrid. Such a scheme offers an innovative route to help meet aspirations of reduced $CO_2$ emissions to the atmosphere for small to medium scale power generation, typical of oil and gas operations.

Our experimental work has confirmed that

- The MCFC technology can act as a $CO_2$ concentrator,
- The MCFC can operate at sub-optimal $CO_2$ levels with limited impact on power output, and
- That NOx has a suppressing, but limited, impact on performance.

## REFERENCES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